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Phase-shift Cavity Ring-down Technique for Detection of NO_2 in PPM Concentration

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ABSTRACT

A phase-shift cavity ring-down spectroscopy (PS-CRDS) experimental set-up has been established using a broadband diode laser for the measurement of phase shift due to absorption of NO_2 in a sealed off cavity ring-down cell. The PS-CRDS technique is verified by optimising various parameters of CRDS cavity and excitation laser. The PS-CRDS signals were measured on the first harmonics using a lock-in-amplifier. The square modulated laser pulses were used in the experiment to obtain the decay time. Measurements of the signal strengths at different CRDS cavity lengths wre also carried out to verify the detection sensitivity for ppm level concentration measurement of trace gases.

Keywords: Phase-shift cavity ring-down spectroscopy, high reflectivity, laser diode, broadband, PS-CDRS technique

1. INTRODUCTION

The phase-shift cavity ring-down spectroscopy (PS-CRDS) is one of the most sensitive techniques for the measurement of the frequency-dependent cross section of molecules. In this technique, absorption coefficient can be measured by the rate at which absorption is taking place by measuring decay time of the light intensity[1-6]. Through this technique, not only the strong absorption region, but also the weak transitions of the molecules can be studied. The PS-CRDS was first introduced by Herbelin[7], *et al.* for the measurement of the reflectivity of the mirrors. The phase shift is recorded for the single pass of a light beam using a lock- in- amplifier[8-10]. In last few years, phase shift CRDS approach has been used in two ways. First approach is based on the alignment of the laser beam along the optical axis of the cavity for which TEM_{00} mode-matching optics is applied. The second approach is based on the off-axis alignment which doesn't require any coupling optics to satisfy the mode-matching criteria. In the first approach, 5 per cent - 20 per cent of the coherent laser beam coupling is reported[11-12]. In the second approach, termed as the cavity enhanced laser spectroscopy, the coupling of the laser beam inside the resonator can be enhanced.

The phase shift-based cavity ring-down laser spectroscopy experiment gives an insight to select the right diode laser power for the detection of traces of NO_2 in the present work. This methodology is quite simple, highly precise, and also a low-cost solution to implement the CRDS experiment for the detection of the molecular species in comparison to the use of the pulsed laser system like Nd:YAG OPO or dye lasers. This technique can be implemented with LED modulation to promote the low-cost solution. To design the compact devices and the gas detection system for the continuous monitoring of toxic gases in the environment due to the rapidly changing gas composition in the mixing ratio, the laser diode provides the ultimate alternative for the trace detection. Though the phase shift method with variable fitting technique and amplitude fitting has been used by Gong[13], *et al.* earlier, they did not study the effect of variable power of the laser diode. In the present work, PS-CRDS technique has been employed in which cavity decay time is obtained using phase-frequency fitting technique. The measurements were repeated for different powers to check the behaviour of the low-to-high laser diode power and at variable distances to select an appropriate cavity length to design a sealed CRDS cell for the trace gas detection. Further, the PS-CRDS technique has been employed for the trace detection of NO_2 gas to observe the effect of different concentrations of NO_2 gas in the balanced mixture of argon by the laser modulation. Though many experiments have been reported for the detection of NO_2 in ppb level concentration by various groups[14] using pulsed laser system by applying algebraic mathematics and by Fast Fourier Transform (FFT), the PS-CRDS experiment with laser modulation techniques makes the trace detection of the NO_2 much simpler.

2. THEORETICAL DESCRIPTION

In the phase-shift CRDS technique, the phase shift is obtained by modulating the laser beam intensity through an optical cavity. The rate of change of laser light (I_{out}) of a given wave number (ω) at the output mirror of the optical cavity is given by Lewis[15], *et al.* as

$$\frac{dI_{out}}{dt} = \frac{1}{\tau} I_{in}(t) e^{-\frac{t}{\tau}} \tag{1}$$

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where I_{in} is the input light intensity.

The decay time constant of the optical cavity is expressed as

$$\tau = \frac{L}{c(1-R+\alpha L)} \tag{2}$$

where L is the cavity length, c is the velocity of light, $R = \sqrt{R_1 R_2}$, with R_1 and R_2 being the reflectivities of the two cavity mirrors, and α is the intra-cavity loss, including the absorption and scattering losses inside the cavity. The modulated intensity in the form of either sine wave or square wave when coupled into the high finesse cavity and reflected back-and-forth times in the cavity produces the output CRD signal with same period as the input laser signal. Both the phase and the amplitude retardation can then be obtained. The CRD signal can be resolved by the series of odd harmonics from which the phase shift can be given by

$$\tan(\phi) = \kappa\omega\tau, \quad \kappa = 1, 3, 5 \ldots\ldots\ldots, \tag{3}$$

where $\kappa = 1$ is used for the fitting of the phase-shift of the first harmonic of the CRD signals.

3. EXPERIMENTAL SET-UP

3.1. PS–CRDS Experiment with Laser Diode

The PS–CRDS experiment was set up with 405 nm laser diode (Vortran) modulation. The concave type mirrors of reflectivity 99.997 per cent at 405 nm with anti-reflection coating with ROC of 1 m purchased from CRD Optics Inc. was chosen for this set-up to improve the quality of the signal. The mirrors were supplied with the test graph for the reflectivity versus wavelength by the manufacturer (CRD Optics Inc.). The reflectivity of the mirrors were further measured employing the cavity ring-down technique as described elsewhere[13,16,17] and was found to be 99.878 per cent with an estimated uncertainty in reflectivity of the order of 10^{-6} , which is close to the values reported[13,16]. The modulated square pulses were obtained using function generator model Rigol DG100 to obtain the PS-CRDS signal. The PS-CRDS signal recorded by the detector (Thorlabs, DET 10A) was further analysed by the lock-in-amplifier (Stanford Research Model SR830) at room temperature. The digital data collected was saved on the computer and calculations were performed using Origin software. The decay time of the photon lifetime inside an optical resonating cavity was recorded for different laser diode powers, ranging from 1 mW to 100 mW and on different distances between 40 cm to 80 cm. Based on these studies, the procedure was further implemented for the detection of gas trace of NO_2 in ppm concentration in a balanced mixture of argon.

3.2 Laser Spectrum Study

The characteristic feature of the Laser diode (Vortran, Stradus 405 nm) at 405 nm, was studied before performing the CW-CRDS experiment by the procedure which has been described in detail elsewhere[17] and is briefly described here. Figure 1 represents the schematic of the experimental set-up used to study the spectral characteristics of the laser diode between 399-410 nm range at 60 mW power of the laser. The laser beam was chopped by the chopper and the on-off pulses in CW laser were generated. Further, the laser intensity was fed to the Holmarc monochromator and the signal at the output was measured by the Thorlabs, DET10 A detector which was then fed to the Stanford lock-in-amplifier for the calibration of the Vortran laser diode. The room temperature was maintained at 21°C during the time of the experiment.

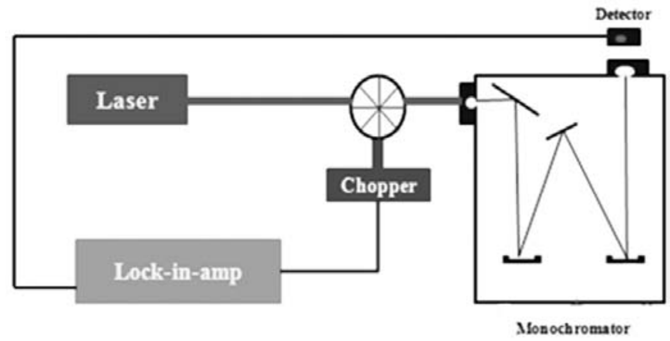

Figure 1. Experimental arrangement for studying of the spectrum of Laser diode using monochromator and Lock-in-amplifier.

3.3 PS-CRDS Experiment for NO_2 Detection

The sealed CRDS cell of 80 cm cavity length was fabricated to perform the PS-CRDS experiment for the trace detection of NO_2 gas in a balanced mixture of argon, the schematic for which is given in Fig. 2. The cavity was fabricated by mild steel (MS) material. The vacuum condition was created inside a sealed cavity ring-down cell. The square wave modulated pulses of the laser diode were used in the CW-CRDS set-up to obtain the CRDS signal. The output trace of the signal was obtained by employing edge state triggered square wave with Si photodiode and the DSO model DL9040 (Yokogawa). Further, the leak signal from CRDS set-up was detected by the detector which was fed to the lock-in-amplifier from Stanford research model SR830 and the phase-shift was measured at first harmonics of the CRD signal. The zero air was purged inside the CRDS cell at 50 mbar pressure from one nozzle controlled by needle valve to avoid any contact of the residual particles on the mirror surface. These after, the vacuum condition was maintained for examining the lifetime of photons inside an optical resonator. The continuous flow of the NO_2 gas mixture of 590 ppm balanced with argon was purged into the CRDS cell at 50 mbar pressure. The laser diode was modulated between

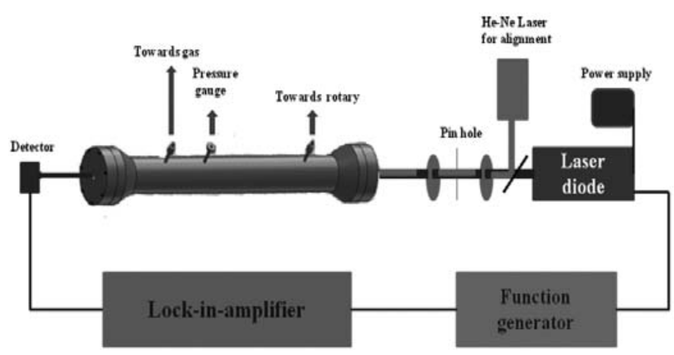

Figure 2. Schematic diagram for the trace detection of NO_2 for three different concentrations in a balanced mixture of argon.

20 kHz to 40 kHz frequency and the power of the laser diode was kept at 60 mW. The phase shift cavity decay time was recorded for the integration time of 60 s by lock-in-amp for a time constant of 100 ms. After recording for 590 ppm of NO_2, the zero air was purged again into the CRDS cell to remove the trace of the existing NO_2 gas and the vacuum condition was maintained again by rotary pump. Further, NO_2 gas at 458 ppm was purged inside the CRDS cell and the PS-CRDS signal was recorded. These steps were repeated for the 185 ppm concentration of the NO_2 gas. The PS-CRDS experiment for the detection of NO_2 gas for three different concentration levels was performed at ambient temperature of 21 °C.

4. RESULTS AND DISCUSSION

The violet diode laser emitting at central wavelength at 405 nm has been used to set-up the PS - CRDS experiment. The diode laser spectrum was measured between 399 nm - 410 nm at 60 mW power and the spectral profile of the laser is shown in Fig. 3. The maximum signal is recorded at 405 nm within the specified range using lock-in-amplifier. The selection of the 405 nm wavelength has been made for the detection of NO_2. It is treated as one of the major precursors to the toxic molecules like nitric acid, ozone and peroxyacyl nitrates. These molecules have direct impact on human health. Apart from this NO_2 is also one of the by-products of explosives.

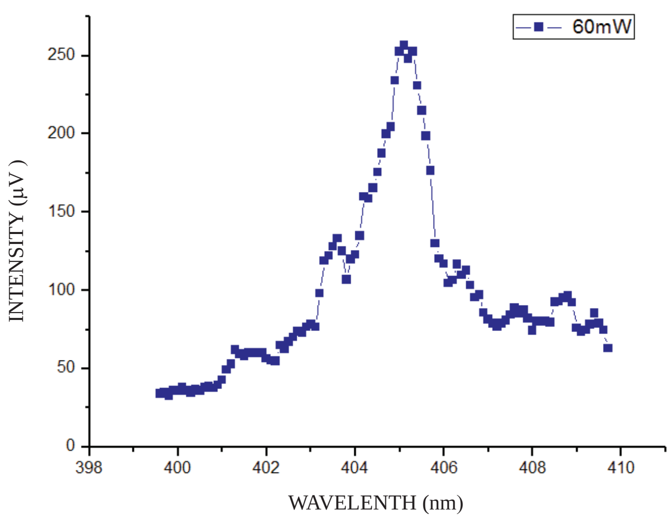

Figure 3. Spectrum of the laser diode recorded between 399 nm to 410 nm.

Figure 4 shows the plot for tangent of phase versus angular frequency of the laser pulses obtained for 1 kHz to 100 kHz using Eqn. (3) at 40 cm cavity length on different power of the laser diode. The slope obtained from these graphs gives the decay time constant of the light intensity for the single-pass absorption of the light. The decay time is then obtained from the slope of the graph plotted between tangent of phase and angular frequency. The same steps are repeated for the PS - CRDS experiment for different powers between 1 mW to 100 mW with an interval of 10 mW at five different distances between 40 cm to 80 cm and the results obtained for the decay time of the light are presented in Table 1. It has been observed that by increasing the power of the diode laser, the decay time

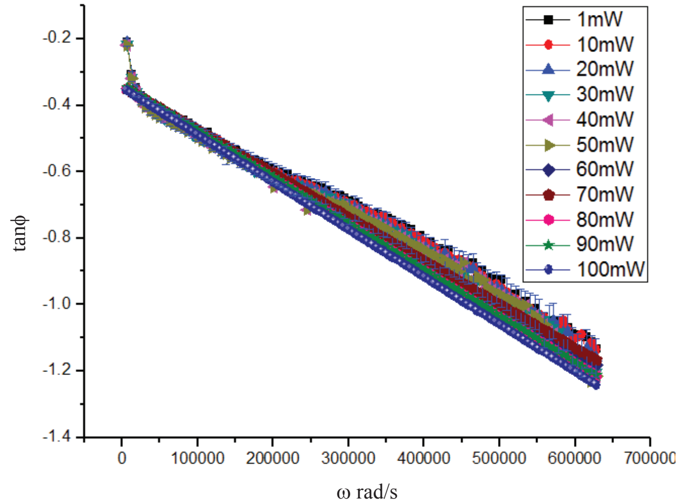

Figure 4. Plots of tangent of phase versus angular frequency at 40 cm cavity length.

was also increased, indicating a rise in high signal-to-noise ratio on higher power. It is concluded that higher laser diode power gives better results for the set-up of single-pass phase shift CRDS technique and the laser power was kept at 60 mW during the second part of the experiment for the detection of NO_2 gas.

The plot of tangent of phase versus angular frequency to obtain the decay times for three different concentrations of NO_2 gas in mixing ratio of argon with 185 ppm, 458 ppm, and 590 ppm flowing through the cavity at 50 mbar is shown in Fig. 5. It has been observed that at the lower concentration, decay time is higher, and on increasing the concentration from 185 ppm to 590 ppm, the decay time was found to decrease. The decay times of the light intensity obtained for three different concentrations of NO_2 are presented in Table 2. The lowest decay time is found to be 10.4 ± 0.4 µs for 590 ppm concentration and it increases with lower concentration and is calculated to be 11.2 ± 0.4 µs and 11.6 ± 0.4 µs for 458 ppm and 185 ppm level of NO_2, respectively. The strong

Table 1. Decay time recorded on different laser diode powers and cavity lengths

Laser diode power (mW)	Cavity length (cm)				
	40	50	60	70	80
1	1.23	1.31	1.15	1.15	1.35
10	1.23	1.23	1.26	1.43	1.18
20	1.25	1.26	1.74	1.21	1.38
30	1.20	1.35	1.48	1.21	1.15
40	1.29	1.37	1.51	1.24	1.46
50	1.29	1.33	1.53	1.27	1.51
60	1.34	1.39	1.58	1.27	1.51
70	1.31	1.41	1.66	1.33	1.57
80	1.39	1.45	1.70	1.40	1.63
90	1.39	1.55	1.76	1.41	1.60
100	1.44	1.54	1.74	1.46	1.51

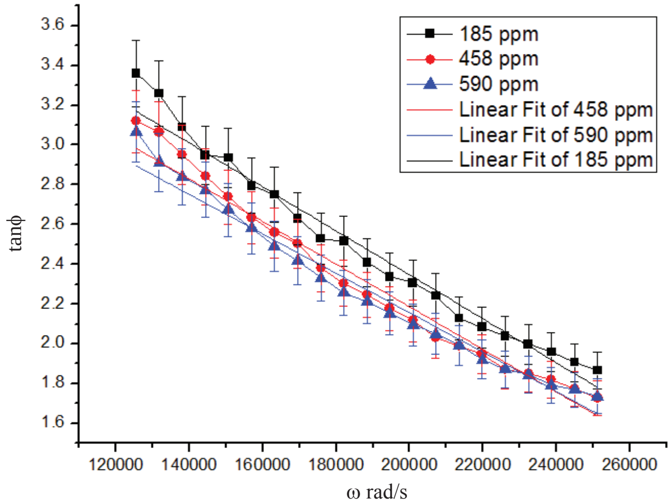

Figure 5. Linear fit decay time plots between tangent of phase and modulation frequencies of laser diode from 20 kHz to 40 kHz for Nitrogen Dioxide gas on different concentrations at 50 mbar pressure.

Table 2. Decay time recorded from the slopes by phase fitting technique for modulation frequencies between 20 kHz to 40 kHz

Concentration (ppm)	Decay Time ± standard error (µs)
185	11.6 ± 0.4
458	11.3± 0.4
590	10.4 ± 0.4

absorption band of NO_2 has its absorption spectrum via two electronic bands as $^2A_1 - {}^2B_1$ and $^2A_1$- $^2B_2$ which covers the wavelength region between 390 nm - 430 nm. In this region the mean cross-section is 6×10^{-9} cm^{-2} varying slightly by ± 40 per cent[18]. The decrease in the value of the decay time is observed which is certainly due to the strong absorption of NO_2 at 405 nm wavelength of the laser diode, which is also the strongest spectral excitation line of the NO_2 gas[19].

So, on increasing the concentration of NO_2, the photon intensity inside an optical resonator gets decreased. These results show that PS-CRDS single pass experiment can be designed for the trace detection of the gases for the lower concentration level of the NO_2 gas in its mixing ratio less than 185 ppm concentration level using the phase fitting technique versus angular frequencies. From above results, this has been verified that PS-CRDS is a convenient and potential technique for detecting the trace gas.

5. CONCLUSIONS

The phase-shift experiment for the PS-CRDS has been used for the measurement of decay time of trace gas filled cavity and to study the effect of the laser and cavity parameters. The phase-shift signals from the CRDS cavity has been recorded using a lock-in-amplifier at the first harmonics of modulation frequency between 20 kHz to 40 kHz. The decay time constant has been determined from the graph plotted for tangent of the phase versus the angular frequency; the slope of which represents the decay time of the cavity. The measurements have been repeated for five different distances and on the variable excitation diode laser powers between 1 mW to 100 mW. In this experiment, it is observed that no saturation effect of the CRDS signal observed up to 100 mW diode laser power. The PS-CRDS signals are measured at three different NO_2 gas in ppm level concentrations to compare the theoretically estimated absorption coefficients for the same set-up. It has been observed that the decay time of the light gets decreased on increasing the concentration. The use of broadband laser diode source with the phase-shift experimental set-up provides a low cost solution for the measurements of ultra-low concentration of trace gases using PS-CRDS technique.

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